

Adsorption of organic molecules may explain growth of newly nucleated clusters and new particle formation

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[1] New particle formation consists of homogeneous nucleation of thermodynamically stable clusters followed by growth of these clusters to a detectable size. For new particle formation to take place, these clusters need to grow sufficiently fast to escape coagulation with preexisting particles. Previous studies indicated that condensation of low-volatility organic vapor may play an important role in the initial growth of the clusters. However, due to the relatively high vapor pressure and partial molar volume of even highly oxidized organic compounds, the strong Kelvin effect may prevent typical ambient organics from condensing on these small clusters. Here we show that the adsorption of organic molecules onto the surface of clusters, not considered previously, may significantly reduce the saturation ratio required for the condensation of organics to occur and therefore may provide a physicochemical explanation for the enhanced initial growth by condensation of organics despite the strong Kelvin effect. **Citation:** Wang, J., and A. S. Wexler (2013), Adsorption of organic molecules may explain growth of newly nucleated clusters and new particle formation, *Geophys. Res. Lett.*, 40, doi:10.1002/grl.50455.

1. Introduction

[2] New particle formation in the atmosphere strongly influences the concentration of atmospheric aerosol particles and therefore their impact on clouds and climate [Kerminen *et al.*, 2005; Laaksonen *et al.*, 2005; Spracklen *et al.*, 2008]. Model simulations show that nearly half of the global cloud condensation nuclei in the planetary boundary layer may be formed through new particle formation [Merikanto *et al.*, 2009]. Formation of stable, long-lived new particles is a two-stage process consisting of homogeneous nucleation of thermodynamically stable clusters followed by the growth of these clusters to a detectable size (i.e., diameter greater than 3 nm) [McMurry *et al.*, 2005]. Due to the large coagulation rate of clusters smaller than 3 nm with the preexisting aerosol population, for new particle formation to take place, these clusters need to grow sufficiently fast to escape removal by coagulation [Kuang *et al.*, 2010]. While some previous modeling and field studies indicated that condensation of low-volatility organic vapors may significantly

enhance the initial growth of the clusters [Kuang *et al.*, 2012; Kulmala *et al.*, 2004c; Paasonen *et al.*, 2010], a physical-chemical explanation is lacking: the strong Kelvin effect at small particle sizes may prevent condensation of even highly oxidized ambient organics due to their the high vapor pressure and partial molar volume [Kulmala *et al.*, 2004a; Zhang and Wexler, 2002]. However, earlier studies did not consider that intermolecular forces between the organic gas phase molecules and nascent clusters may lead to adsorption that substantially alters the growth process under conditions that are subsaturated, with respect to the Kelvin-modified vapor pressure. Here we examine the effect of adsorption on equilibrium saturation ratio over particle surface and the initial growth of the particles.

2. Methods

[3] Traditionally, condensation only occurs when the partial pressure of the condensate in the gas phase exceeds the equilibrium vapor pressure at the particle surface modified by the Kelvin effect, $p_L^\circ \exp\left(\frac{4\sigma v}{RTD}\right)$, where p_L° is the equilibrium vapor pressure over a flat surface (i.e., vapor pressure of the organics in pure liquid or subcooled liquid state). The factor $p_L^\circ \exp\left(\frac{4\sigma v}{RTD}\right)$ describes the enhancement of the surface vapor concentration due to particle curvature (i.e., Kelvin effect), where σ is the surface tension, v is the partial molar volume of the condensing molecule, R is the gas constant, T is the absolute temperature, and D is the particle diameter. The Kelvin term increases exponentially with decreasing D and is huge for 1–2 nm newly formed clusters, reaching as high as 10^5 for typical ambient organic species [Kulmala *et al.*, 2004a; Zhang and Wexler, 2002]. Given the relatively large vapor pressure and large partial molar volume of even highly oxidized organic compounds, under typical atmospheric conditions, organic vapors cannot contribute to the growth of small clusters by traditional condensation due to the strong Kelvin effect. Other mechanisms have been proposed to explain the observed particle formation and growth, including heterogeneous chemical reactions [Zhang and Wexler, 2002], the lowering of vapor pressure through Raoult's law [Kulmala *et al.*, 2004a; Kulmala *et al.*, 2004b] (nano-Kohler theory), and particle number fluxes due to heterogeneous nucleation [Wang *et al.*, 2012].

[4] Adsorption of organics onto surfaces occurs under subsaturated conditions due to the intermolecular forces between the organic molecule and the surface. Such adsorption has been described by a number of isotherms including Langmuir, Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-de Boer [e.g., Adamson and Gast, 1997]. These same isotherms and their extensions have also been used to model bulk solution thermodynamics by

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assuming that solutes behave as surfaces in solution-sorbing solvent [Dutcher *et al.*, 2011]. BET and Frenkel-Halsey-Hill isotherms were also employed to describe the adsorption of water molecules onto the surfaces of wettable insoluble particles and its impact on cloud droplet activation [Henson, 2007; Sorjamaa and Laaksonen, 2007]. Here we are interested in modeling the behavior of clusters and nanoparticles, where the surface and bulk are not necessarily distinguishable from each other. That BET isotherms have been used to successfully model both surfaces and bulk solutions lends credence to (a) its application where the surface and bulk are merged and (b) it accurately represents intermolecular forces between clusters and organic molecules.

2.1. BET Isotherm and the Equilibrium Saturation Ratio Above Growing Particle Surface

[5] The BET isotherm is given by

$$\theta = \left(\frac{1}{1-x} \right) \left(\frac{cx}{1-x+cx} \right) \quad (1)$$

where θ is the fractional coverage of the surface by the adsorbed molecule, in layers, x is the activity of the adsorbing molecule in the gas phase and c is a temperature-dependent parameter. The activity of the adsorbing molecule can be expressed as its partial pressure divided by its equilibrium vapor pressure over a flat surface, $x = p/p_L^\circ$. Equation (1) can be solved for x to obtain:

$$x = \frac{p}{p_L^\circ} = \frac{[c - \theta(c-2)] - \sqrt{c^2(\theta-1)^2 + 4\theta c}}{2\theta(1-c)} \quad (2)$$

[6] The constant c is given by [Dutcher *et al.*, 2010; Pradas *et al.*, 2004]:

$$c = \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left[\frac{-(\Delta G_{\text{ads}} - \Delta G_{\text{liq}})}{RT}\right] \quad (3)$$

where ΔG_{ads} is the adsorption free energy of organic molecules on the sites at the cluster surface (i.e., first layer), and ΔG_{liq} is the adsorption free energy of organic molecules onto the multilayer (i.e., liquefaction).

[7] The Kelvin effect must also be considered for small clusters since it substantially increases vapor pressure over the particle surface. As a result, the equilibrium saturation ratio over the growing cluster/particle with diameter of D becomes:

$$S = \frac{p(D)}{p_L^\circ} = \frac{[c - \theta(c-2)] - \sqrt{c^2(\theta-1)^2 + 4\theta c}}{2\theta(1-c)} \cdot \exp\left(\frac{4v\sigma}{RTD}\right) \quad (4)$$

[8] Here we assume that the adsorbed organic molecules do not form an ideal solution with the inorganic species inside the clusters. Instead, the particles maintain a core (initial cluster)/shell (organics) structure. The major inorganic species inside freshly nucleated clusters are likely sulfate. Under typical ambient relative humidity (RH), some water is likely associated with the initial clusters. However, the solubility of organics is very low except for very polar compounds, such as small organic acid. Furthermore, given the relatively lower surface tension of organic compounds, we expect the adsorbed organics to remain at the particle surface [Chen *et al.*, 2002; Wyslouzil *et al.*, 2006].

[9] The coverage θ can be derived using the following approach. The number of organic molecules adsorbed to the “core” cluster can be related to its diameter, D_{core} , and the diameter after adsorption, D , by:

$$N = \frac{\frac{\pi}{6}D^3 - \frac{\pi}{6}D_{\text{core}}^3}{\frac{\pi}{6}d_o^3} = \frac{D^3 - D_{\text{core}}^3}{d_o^3} \quad (5)$$

where d_o is the diameter of organic molecule and can be estimated from its partial molar volume. The coverage is then given by:

$$\theta = N \frac{\frac{\pi}{4}d_o^2}{\pi D_{\text{core}}^2} = \frac{D^3 - D_{\text{core}}^3}{d_o^3} \frac{d_o^2}{4D_{\text{core}}^2} \quad (6)$$

[10] Combining equations (4) and (6), we can then calculate S , the equilibrium saturation ratio over particle surface, as a function of particle diameter, D .

2.2. Estimation of ΔG

[11] Here ΔG is estimated using the data on the adsorption of organics on sulfate particles published in earlier studies [Liang *et al.*, 1997]. In these studies, the adsorption of organics was examined under dilute regime where θ linearly depends on p , corresponding to $x \ll 1$. The Kelvin effect was minor due to large particles sizes employed, so for the conditions of these experiments, equation (1) may be simplified to:

$$\theta = cx = \frac{p}{p_L^\circ} \exp\left(-\frac{\Delta G}{RT}\right) \quad (7)$$

[12] A surface-area normalized gas-particle phase partitioning coefficient $K_{p,s}$ may be defined as [Liang *et al.*, 1997]:

$$K_{p,s} = \frac{\Gamma}{C} = \frac{\theta\Gamma_m}{C} \quad (8)$$

where Γ is the surface concentration of adsorbed molecule, C is its gas phase concentration, and Γ_m is the surface concentration for a complete monolayer. Γ_m can be estimated by:

$$\Gamma_m = \frac{1}{A_m} \quad (9)$$

where A_m is the surface area occupied by a single adsorbed molecule. The ideal gas law can be used to relate the gas phase concentration, C , to its partial pressure:

$$C = p/kT \quad (10)$$

where k is the Boltzmann constant.

[13] By combining equations (7)–(10), we have:

$$\Delta G = -RT \left[\ln K_{p,s} + \ln p_L^\circ + \ln \left(\frac{A_m}{kT} \right) \right] \quad (11)$$

Table 1. Parameters Used in Simulations of the Equilibrium Saturation Ratio Above the Surface of Growing Particles

Parameter	Value
σ	0.04 N/m
v	135 cm ³ /mol
T	293.15 K
ΔG	-10, -5, 0, 5, 10 kJ/mol

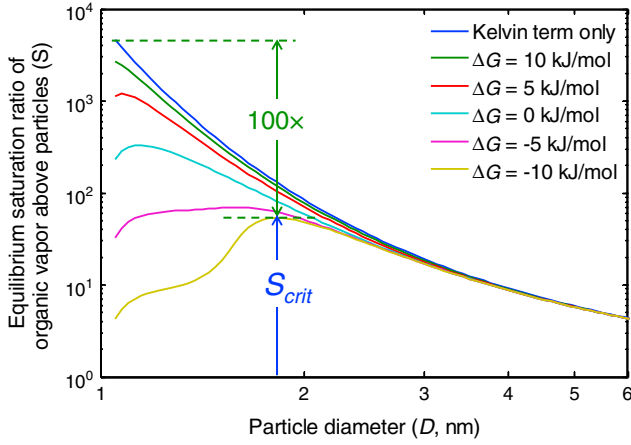


Figure 1. Equilibrium saturation ratio over growing particle surface for the Kelvin effect only and for the inclusion of adsorption.

[14] Liang *et al.* [1997] examined the adsorption of n-alkanes and polynuclear aromatic hydrocarbons (PAHs) on dry ammonium sulfate particles in an outdoor chamber. For the adsorption of PAH on sulfate particles, Liang obtained the following linear regression for adsorption under RH of 42%:

$$\ln K_{p,s} = -1.04 \times \ln p_L^\circ - 2.856 \quad (12)$$

[15] Note that equation (11) is rewritten from the original equation in Liang *et al.* [1997] using the natural logarithm and converting the units of p_L° from Torr to Pascal. Combining equations (11) and (12) gives:

$$\Delta G = -RT \left[-0.04 \times \ln p_L^\circ - 2.856 + \ln \left(\frac{A_m}{kT} \right) \right] \quad (13)$$

[16] Similarly for the adsorption of n-alkanes on ammonium sulfate particles, Liang *et al.* [1997] obtained the following linear regression:

$$\ln K_{p,s} = -0.96 \times \ln p_L^\circ - 2.923 \quad (16)$$

giving:

$$\Delta G = -RT \left[0.04 \times \ln p_L^\circ - 2.923 + \ln \left(\frac{A_m}{kT} \right) \right] \quad (17)$$

[17] The saturation vapor concentration of organic compounds participating in the early particle growth is likely less than 10^6 cm^{-3} [Anttila and Kerminen, 2003; Kerminen *et al.*, 2000; Kulmala *et al.*, 1998], which corresponds to p_L° of less than $4 \times 10^{-9} \text{ Pa}$ at $T = 298.15 \text{ K}$. Assuming $p_L^\circ = 4 \times 10^{-9} \text{ Pa}$ and $A_m = 100 \text{ \AA}^2$, then from equations (15) and (17) $\Delta G(298.15 \text{ K}) = -8.45 \text{ kJ/mol}$ for PAHs and $\Delta G(298.15 \text{ K}) = -4.45 \text{ kJ/mol}$ for n-alkanes, respectively. If instead, $A_m = 25 \text{ \AA}^2$, $\Delta G(298.15 \text{ K}) = -5.02 \text{ kJ/mol}$ and $\Delta G(298.15 \text{ K}) = -1.02 \text{ kJ/mol}$ for adsorption of PAH and n-alkanes, respectively. While the above systems may not represent all the adsorbing organic species nor the cluster surfaces, the results suggest that ΔG is typically on the order of several kJ/mol and may be negative for the adsorption of organic compounds on inorganic salts.

4. Results

[18] To examine the impact of adsorption on initial particle growth, we calculated the equilibrium saturation ratio (S) over a growing particle as a function of particle diameter using equations (4) and (6) and parameters (Table 1) that are within the typical ranges. Figure 1 shows the results for D_{core} of 1 nm and ΔG ranging from -10 to 10 kJ/mol . Also shown is the equilibrium S when the effect of adsorption is neglected (i.e., only the Kelvin effect is included). Adsorption due to the intermolecular forces between the organic molecule and particle surface appears to significantly reduce the equilibrium vapor pressure [McGraw *et al.*, 2012], therefore facilitating the initial growth of small clusters despite their strong Kelvin effect. The decrease of equilibrium saturation ratio S is most significant for the initial particle growth (i.e., when particle diameter is less than $\sim 2 \text{ nm}$) and results in the reduction of the minimum S (S_{crit}) that is required for the particles to grow. The reduction of S_{crit} depends on the value of ΔG . For ΔG values in the range of about -5 to -10 kJ/mol , adsorption reduces S_{crit} by a factor of more than 100 (i.e., from ~ 6000 to ~ 50). At $\Delta G = 0$, the reduction in S_{crit} is less pronounced but remains significant at ~ 10 . As ΔG approaches 10 kJ/mol , the impact of adsorption on S_{crit} becomes quite minor. It is worth noting that at particle sizes greater than 3 nm , equilibrium S calculated using different ΔG values are essentially the same as that for Kelvin term only, suggesting minor impact of adsorption following the initial particle growth (Figure 2).

[19] S_{crit} is also examined as a function of ΔG for D_{core} ranging from 1 to 10 nm . The results indicate that S_{crit} is sensitive to ΔG when $-5 \text{ kJ/mol} < \Delta G < 10 \text{ kJ/mol}$ and is the lowest when $\Delta G < -5 \text{ kJ/mol}$. These values of ΔG are similar to the range estimated above. For example, when $D_{\text{core}} = 1 \text{ nm}$, S_{crit} remains nearly constant at 50 when ΔG is less than -5 kJ/mol . As ΔG increases above -5 kJ/mol , S_{crit} increases strongly with ΔG , and approaches 6000, the limit when adsorption is not considered, at $\Delta G = \sim 25 \text{ kJ/mol}$. It is evident that the impact of adsorption on S_{crit} is most pronounced for small D_{core} (i.e., less than a few nanometers), again suggesting that adsorption may strongly influence initial particle growth but likely has a minor impact afterward.

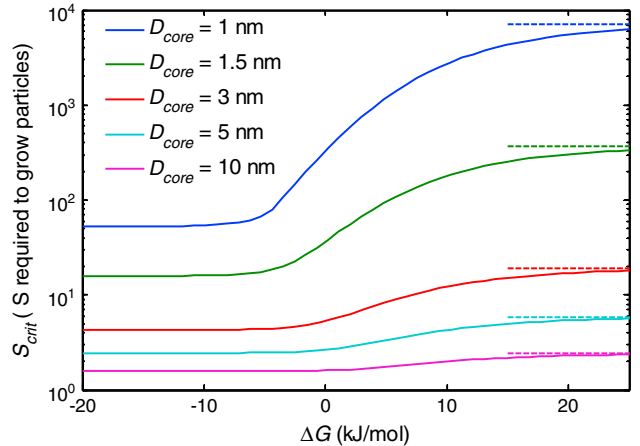


Figure 2. Critical supersaturation as a function of ΔG for core diameter ranging from 1 to 10 nm . The dashed lines represent S_{crit} for the case where adsorption is not considered.

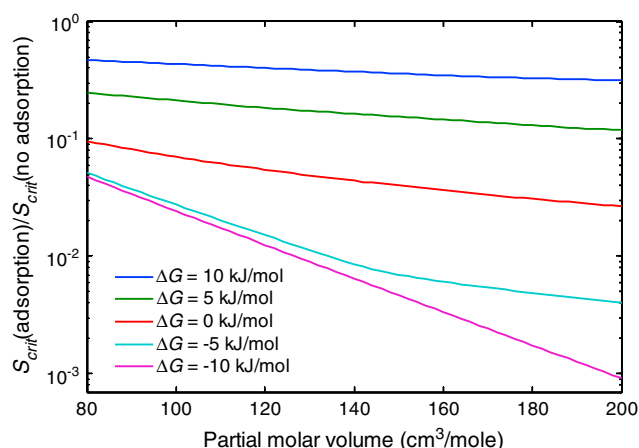


Figure 3. The ratio of S_{crit} with adsorption to that without adsorption as a function of partial molar volume for D_{core} of 1 nm.

[20] In addition to its dependence on ΔG , S_{crit} is also a function of the condensing species via its partial molar volume and its effect on surface tension. Surface tension only plays a role in the Kelvin term, but the partial molar volume also determines the size of the condensing molecules, d_o and therefore the derived θ (i.e., equation (6)), which was used to calculate the adsorption term (i.e., the first term on the right side of equation (4)). The influence of v on the adsorption term is very small compared to that on the Kelvin term; therefore, σ and v essentially play the same role on S_{crit} . Figure 3 shows the ratio of S_{crit} with adsorption to that without adsorption as a function of v for $D_{\text{core}} = 1$ nm and all other parameters (except for v), the same as in Table 1.

[21] For given ΔG and D_{core} values, the reduction in S_{crit} due to adsorption becomes more pronounced as σ or v (i.e., the Kelvin effect) increases, especially when ΔG is less than ~ -5 kJ/mol. For example, when $\Delta G = -10$ kJ/mol, adsorption reduces S_{crit} by a factor of ~ 20 when $v = 80$ cm³/mol, and the reduction reaches a factor of ~ 1000 when v increases to 200 cm³/mol. In contrast, when $\Delta G = 0$ kJ/mol, the reduction in S_{crit} only varied from a factor of 10 to 30 when v increases from 80 to 200 cm³/mol.

5. Conclusions

[22] Here we show the adsorption due to the intermolecular forces between organic molecules and particle surface may significantly decrease the equilibrium vapor pressure, thereby reducing the minimum saturation ratio required for the organics to contribute to the initial growth of small clusters during new particle formation events. The reduction of S_{crit} is most pronounced when ΔG is less than -5 kJ/mol and strongly depends on the ΔG when -5 kJ/mol $< \Delta G < 10$ kJ/mol. For core cluster diameter of 1 nm, S_{crit} may be reduced by a factor of up to 100 when adsorption is included. The impact of adsorption on S_{crit} is most pronounced for D_{core} less than a few nanometers, suggesting that adsorption may strongly influence initial particle growth, but likely has a minor impact afterward. The value of ΔG was estimated using data collected in previous smog chamber studies and ranges from -8 to -1 kJ/mol for the adsorption of organics, including PAHs and α -alkanes on sulfate particles. While these systems do not represent all the adsorbing organic species nor the

cluster compositions, measurements suggest that ΔG is the on the order of several kJ/mol, is likely negative, and therefore may lead to significant reduction of S_{crit} . This may provide a physicochemical explanation for the enhanced initial growth by condensation of organics despite the strong Kelvin effect. The value of ΔG needs to be quantified in future studies in order to better understand the effect of the adsorption of ambient organics on the initial growth of the newly formed clusters.

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